Aluminum desmutting agent

Patent number:	GB2000525
Publication date:	1979-01-10
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Classification:	
- international:	C23G1/12
- european:	B41N3/03S, C23G1/12B
Application number:	GB19780027873 19780626
Priority number(s):	JP19770075022 19770624

Also published as:

JP54010234 (A)
FR2395304 (A1)

Abstract of **GB2000525**

An aqueous solution of a persulfate and sulfuric acid effectively removes smut formed on the surface of an aluminum sheet as the result of surface etching processes.

(12) UK Patent Application (19) GB (11) 2 000 525 A

(21) Application No 7827873
(22) Date of filing 26 Jun 1978
(23) Claims filed 26 Jun 1978
(30) Priority data
(33) Japan (JP)
(43) Application published
10 Jan 1979
(51) INT CL[2]
C23G 1/12
(52) Domestic classification
C7E 118 152 172
192 194 208 214 3B
(56) Documents cited
GB 1399111
GB 478209
GB 360126
(58) Field of search
C7E
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(54) Aluminum desmutting agent

(57) An aqueous solution of a persulfate and sulfuric acid effectively removes smut formed on the surface of an aluminum sheet as the result of surface etching processes.

GB2 000 525 A

SPECIFICAION

Aluminium Desmutting Agent

This invention relates to a process for the removal of smut that is formed as a by-product of the etching of the surface of sheets of aluminum or the alloys of aluminum.

An aluminum surface which is to form the base of a lithographic printing plate is ordinarily etched with an aqueous solution of an acid of alkali for the purpose of removing the solvents, emulsions, surface active agents, oxide films, scales and other impuritles inherent to the manufacturing methods employed in producing commercial aluminum sheets. Such etching is useful to remove smears incorporated into the aluminum, effects a smoothening of the sandy surface of aluminum, elimantes luster from the aluminum surface and promotes a uniformity of the same.

Examples of the aforementioned acids and alkalis include fluoric acid, fluroidized zirconic acid, phosphoric acid, hydrochloric acid, sulfuric acid, acetic acid, other inorganic acids and organic acids, potassium hydroxide, sodiu hydroxide, tri-sodium phosphate, sodium carbonate, and sodium aluminate. It is possible to employ the acidic salts instead of the acids, and it also possible to employ alkaline salts instead of alkalis.

It is possible to cause the etching solution to contain a third solution such as a neutral salt, a surface active agent, a scale preventive agent, etc. It is customary that the etching treatment is carried out by using a one to ten per cent by weight aqueous solution of alkali at a solution temperature in the range of between 40 and 90 degrees centigrade for a period of three seconds to ten minutes.

When the surface of aluminum is etched by using the aqueous solution of such an acis or alkali, however, a black, insoluble residue or smut is produced on the surface thereof. In the case where a film or coated film is to be provided on this aluminium surface which has smut thereon, the smut effects an undesirable interference with the film and the undesirable properties tend to increase as the etching time increases. As a result, it becomes extremely important to eliminate the smut in the cases where a substrate for printing plates, paintings, enamel plating or photoresists are to be obtained.

This treatment for the elimination of smut is called the desmutting process. The agent which is used for such a desmutting treatment is called a desmutting agent. As the desmutting agents, phosphoric acid, nitric acid, chromic acid or hydrogen fluoride, have been used either individually or as a mixture. As the desmutting agents for aluminum, the high-concentration solution of a mixture of nitric acid and chromic acid is also widely employed. However, the desmutting treatments using the aforementioned desmutting agents have the following shortcomings:

1. Since the desmutting agent is in the form of a highly concentrated aqueous solution, it requires a large amount of an alkali for neutralization prior to discarding.
2. Since the hexavalent chromium ions are harmful to the human body, the treatment for its subsequent disposal is extremely complicated.
3. In the case where high temperature nitric acid or sulfuric acid is employed, a malodorous gas is generated.
4. It is adversely affected by the concentration of metallic ions in the smut which is dissolved in the desmutting agent.

It is possible to markedly improve the product quality, productivity, economy, pollution and operability by surmounting these shortcomings. Accordingly, the purpose of this invention lies in providing a process for desmutting in which a solution of an acid at a low concentration is employed to satisfactorily carry out desmutting operation, without containing such heavy metal ions as are harmful to the human body and without having a malodor.

This invention relates to a process for desmutting which is characterized in that the smut which is produced on the surface of aluminum which is the result of an etching treatment is removed by using a desmutting agent containing a persulfate and sulfuric acid in relatively dilute concentrations.

The desmutting process of this invention will be described in detail in connection with the surface treatment of aluminum.

A surface of an aluminum sheet is etched by using either an acid or an alkali as heretofore described. This etching treatment can be carried out in conformity with the conventional methods which are well known in the art and not a point of novelty here. The aluminum which results from this etching treatment is then, if necessary, rinsed with water. In the case where etching is carried out with an alkali, in particular, it is desirable that cleaning with water be carried out sufficiently until the cleaning water no longer shows any alkalinity.

For cleaning with water, there are various methods known, including, for example, immersion treatment, cleaning with running water and water spraying, etc.

The time which is considered to be sufficient to carry out the aforementioned water cleaning is ordinarily in a range between approximately three seconds and five minutes in the case of the immersion treatment, and in a range between approximately three seconds and five minutes in the case of cleaning with running water and cleaning with a water spray.

The aluminum which has been given an etching and cleaning treatment in this manner is then given a desmutting treatment in accordance with the process of this invention, with the result that the smut which has been produced in connection with the etching treatment is removed.

According to the desmutting process of this invention, the smut is removed by using an aqueous solution consisting of a persulfate and sulfuric acid. The persulfates according to this invention may be, for example, heavy metal salts. Among these, the alkali metal slats and ammonium salts are preferable and, among these, desirable salts are specifically sodium salts, potassium salts and ammonium salts.

The effective concentration of the persulfate can be 0.1 per cent or higher. It should preferably be in the range between 0.2 and 7.0 per cent when it is used on an industrial scale. More desirably, it should be in the range between 0.3 and 5.0 per cent.

The density of sulfuric acid can be 0.3 per cent or higher in order to be effective. It should preferably be in the range between 0.4 and 5.0 per cent and, more desirably, in the range between 0.5 and 2.5 per cent. The lower limits of these compounds are determined by the desmutting ability and the upper limits thereof are determined by the cost of the treatment.

In this invention, the aforementioned two ingredients provided a sufficient amount of desmutting ability. However, it is possible to add a surface active agent and/or an organic solvent, if desired.

Organic solvents which can be added include such alcohols as methanol, ethanol, isopropanol, diacetone alcohol; such ketones as acetone, methyl ethyl ketone; such blycol ethers as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, dioxane, tetrahydrofurane, evaporative oil or light oil, either individually or in combinations.

In the case where a surface active agent is added, its amount is less than 0.1 per cent and preferably less than 0.05 per cent. In the case where an organic solvent is added, its amount is less than one per cent and preferably less than 0.5 per cent.

It is preferred for the pH of an aqueous desmutting solution, according to this invention, to be 3.7 or less; the pH should more preferably be two or less and most preferably 1.5 or less.

According to this invention, it is preferred for a metal ion to be employed to some extent in the desmutting system as a whole. A desmutting agent requires oxygen in its operation and it is thus possible to oxidize and remove the smut.

Since the aluminum plate which as been treated according to this invention has an extremely clean surface, such a surface is particularly useful for producing printing plates, name plates, printed wiring, etc. In particular, such treatment is extremely effective when used for the preparation of aluminum sheets to be employed as presensitized printing plates.

The aluminum which is given a surface treatment in accordance with the desmutting process according to this invention includes pure aluminum and aluminum alloys. Various aluminum alloys can be used; they are, for example, aluminum alloys with such metals as silicon, copper, manganese, magnesium, chromium, zinc, lead, bismuth, nickel, etc. The examples of aluminum alloys will be described below. The unit used in the table is weight per cent and the remainder is aluminum.

Aluminum Alloy	*Si*	*Cu*	*Mn*	*Mg*	*Cr*	*Zn*
2S	0.4	–	–	0.6	–	–
3S	–	–	1.2	–	–	–
24S	–	4.5	0.6	1.5	–	–
52S	–	–	–	2.5	0.25	–
81S	0.6	0.25	–	1.0	0.25	–
75S	–	1.60	–	2.50	0.30	5.60

These compositions include some quantity of iron and titanium and a negligible amount of impurities that are not indicated in the table.

This invention will be more clearly demonstrated in the following examples. In these examples, the term "per cent" in each of the examples indicates "weight per cent." It is mentioned, further, that the effectiveness of the desmutting treatment was determined in accordance with the following testing method.

Testing Method

An aluminum plate which has been etched and given a desmutting treatment according to the process of this invention was immersed in an aqueous solution of five per cent sodium silicate, at the temperature of 70 degrees centigrade for a period of one minute. After it was cleaned with water for a period of one minute with running water at 20 degrees centigrade, it was dried. This aluminum plate was coated with a photosensitive solution having the following composition to a thickness of approximately 1.0 gram per square meter: shellac 20 grams; diazo resin (p-toluene sulfonate of a condensate of p-diazo diphenyl amine and formaldehyde) 0.5 grams; dye (Crystal Violet) 0.1 gram; and 2-methoxy ethanol 100 grams.

This plate was dried at the temperature of 100 degrees centigrade for a period of two minutes, thereby obtaining a photosensitive printing plate.

This photosensitive printing plate was exposed to light by using a two kilowatt metal halide lamp as a light source for a period of 60 seconds at a distance of 60 centimeters. After it was immersed for a period of 30 seconds in a developing solution containing 20 grams of isopropyl alcohol and 80 grams of water, it was lightly wiped with sponge for the purpose of developing. The number of "voids" or spots where the photosensitive composition did not adhere to aluminium was observed. The desmutting treatment is considered incomplete when such voids appear, whereas the desmutting treatment is effective when such void

spots do not appear at all. In orther words, at such "void" locations, the smut did not allow the photosensitive coating to reach and ahere to the base aluminum.

In the examples, the codes 0, # and cross have the following meanings:

A white circle: without "voids" and there is an excellent desmutting treatment.

A # sign: there are some "voids", there is some desmutting treatment ability.

A cross: there are many "voids" and there is no effective desmutting treatment ability.

Example 1

0.04 square meters of 3S aluminum whose thickness was 0.24 millimeters was grained by using the method which is described in the Japanese Patent Disclosure No. Sho 48–49501. After this, it was immersed in a two per cent potassium hydroxide aqueous etching solution at 60 degrees centigrade for a period of 30 seconds, and this was followed by cleaning with water.

The surface of aluminum was black with smut. This aluminum plate was immersed in a desmutting solution, as described in the following table. After a treatment with sodium silicate, the coating of the developing solution, exposure to light and developing were carried out. The composition of the desmutting solution included sodium persulfate and sulfuric acid. The combination of these two ingredients is shown in the following Table 1. As the desmutting solution, water was added to the two ingredients to make the entire volume one kilogram.

Table 1

Sulfuric Acid / Sodium Persulfate	0 grams	1g	2g	3g	10g	50g	70g
0grams	x	x	x	x	x	x	x
1 g	x	#	#	#	#	#	#
3 g	x	0	0	0	0	0	0
5 g	x	0	0	0	0	0	0
10 g	x	0	0	0	0	0	0
25 g	x	0	0	0	0	0	0
50 g	x	0	0	0	0	0	0
100 g	x	0	0	0	0	0	0

Example 2

An aluminum plate whose thickness was 0.2 millimeters (3S) was immersed for a period of two minutes at the temperature of 70 degrees centigrade in an aqueous solution of eight per cent trisodium phosphate (12 hydrate), and thereafter it was cleaned with running water whose temperature was 20 degrees centigrade for a period of one minute. It was then immersed for a period of one minute in a desmutting agent having the following composition: potassium persulfate 20 grams; sulfuric acid 20 grams; and water 960 grams. As a result, the black smut was removed and a white aluminium surface was obtained.

This aluminum plate was cleaned with running water whose temperature was 20 degrees centigrade for a period of one minute.

Thereafter, a sodium silicate treatment was carried out. Further, coating, exposure to light and developing were carried out. As a result, no "voids" were observed.

As comparison with the above result, a superior printing plate without any "voids" was also obtained in the case where a 10N nitric acid aqueous solution was substituted as a desmutting agent. However, the amount of an alkali for neutralization which was required for the waste water treatment of this nitric acid desmutting agent was approximately 25 times as much as that required in the case of the aforemention desmutting agent of the present invention.

Moreover, the 10N nitric acid aqueous solution generated malodorous gas and, at the same time, it turned yellow or was deteriorated when it adhered to the human body or clothes. However, the aforementioned desmutting agent of the present invention did not develop any malodor nor did it develop any adverse effect when the human body was partially immersed in the solution. Its operability and safety were extremely satisfactory.

When a desmutting agent which was prepared by mixing 100 grams of 36N concentrated sulfuric acid, 200 grams of chromic acid and 700 grams of water was used instead of the aforementioned desmutting agent of the present invention, there developed innumerably spots on the surface of aluminum, probably due to the fact that chromium remains on the aluminum surface at the time when the anodic oxide film was formed. By using this aluminum plate, a printing plate was prepared in the same manner. It was found that developing was not carried out satisfactorily at those portions where spots were produced.

In addition, this desmutting agent of sulfuric acid-chromic acid is necessarily prepared by using the stage where hexavalent chromium ions were reduced to trivalent ions by means of ferrous sulfate in the case where a waste water treatment is carried out. The same is neutralized with potassium hydroxide and the

precipitate produced is filtered. Accordingly, the waste water treatment is much more complicated than that required for the desmutting agent of the present invention.

CLAIMS

1. A composition for desmutting the etched surface of a sheet of aluminum or aluminum alloy which comprises an aqueous solution of sulfuric acid and a persulfate.

2. A composition as claimed in claim 1 wherein the persulfate is selected from heavy metal salts, alkali metal salts, alkali earth metal salts and ammonium salts.

3. A compsoition as claimed in claim 1 or claim 2 wherein the persulfate is selected from sodium persulfate, potassium persulfate and ammonium persulfate.

4. A composition as claimed in any one of claims 1 to 3 wherein the concentration of persulfate is at least 0.1 per cent by weight.

5. A composition as claimed in claim 4 wherein the concentration of persulfate is from about 0.1 to about 7.0 per cent by weight.

6. A composition as claimed in claim 5 wherein the concentration of persulfate is between 0.2 and 7 percent.

7. A composition as claimed in claim 6 wherein the concentration of persulfate is between 0.3 and 5.0 percent.

8. A composition as claimed in any one of claims 1 to 7 wherein the concentration of sulfuric acid is at least 0.3 per cent by weight.

9. A composition as claimed in claim 8 wherein the concentration of sulfuric acid is from about 0.3 to about 5.0 per cent by weight.

10. A composition as claimed in claim 9 wherein the concentration of sulfuric acid is between 0.4 and 5.0 per cent.

11. A composition as claimed in claim 10 wherein the concentration of sulfuric acid is between 0.5 and 2.5 per cent.

12. A composition as claimed in any one of claims 1 to 11 which also comprises a surface active agent and/or organic solvent.

13. A composition as claimed in claim 1 and substantially as hereinbefore with reference to any one of the Examples.

14. A process for desmutting the etched surface of aluminum, which comprises contacting the aluminum with a composition as claimed in any one of claims 1 to 13.

15. Aluminum whenever treated by a process as claimed in claim 14.

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Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon Surrey, 1978.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.